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(56) Documents Cited
US 5319018 A US 4870197 A

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(54) Stainproof resin composition

(57) A stainproof resin composition comprises as an active ingredient a resin having at least one metal carboxylate group represented by the following formula:

Rp-COO-M-OH (A)

wherein Rp is a substrate resin and M is a divalent metal atom.

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STAINPROOF RESIN COMPOSITION AND PRODUCTION METHOD THEREFOR

This invention relates to a stainproof composition comprising as an active ingredient a resin having at least one metal carboxylate group and a production method therefor.

Heretofore, resins having a metal salt structure in the molecule have been studied and used as binders for stainproof coatings. The most common resin having such a structure in the molecule is tin carboxylate. However, since the toxicity of tin carboxylate has been called in question, copper and zinc carboxylates have been used in recent years. These resins usually are represented by the following general formula (B) or (C):

$$Rp\text{-}COO\text{-}M\text{-}(R)_n \qquad (B)$$

$$Rp\text{-}COO\text{-}M\text{-}(OCOR)_n \qquad (C)$$

wherein Rp is a substrate resin, M is a divalent metal atom, R is a hydrocarbon group, and n is an integer of 1 to 3.

If a resin includes a hydroxyl group, traditionally such resins tend to gel during synthesis and become defective as stainproof resin compositions.

The synthesis of the compound of the formula (B) is costly and the synthesis of the compound (C) involves extremely high costs for purification because a mixture of various compounds is readily produced due to the small difference of reactivity between the two or more hydroxyl groups which are present.

It is therefore an object of the present invention to provide a stainproof resin composition having at least one metal carboxylate group and a production method therefor. It is also an object to provide a resin having excellent antibiotic stainproofing properties which is suitable for

use in stainproof coatings.

In accordance with these objectives there is provided a stainproof resin composition comprising as an active ingredient a resin having at least one metal carboxylate group represented by the formula:

Rp-COO-M-OH

wherein Rp is a substrate resin and M is a divalent metal atom.

In further accordance with these objectives, there is provided a method for producing a stainproof resin composition comprising as an active ingredient a resin having at least one metal carboxylate group represented by the formula:

Rp-COO-M-OH (A)

wherein Rp is a substrate resin and M is a divalent metal atom, the method comprising reacting a resin having at least one carboxyl group with a divalent metal oxide or a divalent metal hydroxide in the presence of water.

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by the means and combinations particularly pointed out in the appended claims.

In a preferred embodiment of the present invention, the divalent metal atom of the resin composition comprises at least one metal selected from copper, zinc, calcium, magnesium and iron. The substrate resin may be any resin having at least one carboxyl group and is preferably a vinyl polymer having an acid value of 30 to 300.

The inventors of the present invention have conducted intensive studies on an inexpensive stainproof resin composition having at least one metal carboxylate group and

a production method therefor, and have found that a resin having the structure of the above general formula (A) can be synthesized without gelation by reacting a resin having at least one carboxyl group with a divalent metal oxide or hydroxide in the presence of water.

Generally, a three-dimensional structure may be generated by ion bonding when a divalent metal atom is employed. Surprisingly, gelation does not occur in the method according to the present invention when the resin is reacted with preferably 0.1 to 1 mol of a divalent metal oxide or divalent metal hydroxide for every 1 mol of the carboxyl group. In addition, the presence of a small amount of water may prevent the generation of a three-dimensional structure caused by ion bonding.

When there is 0.1 mol or less of water present for every 1 mol of carboxyl group present, structural viscosity may develop with the result being a likely increase in the viscosity of the resin. When 1 mol or more of water is present, excess water should be separated. Therefore, it is preferable that 0.1 mol to 1 mol of water be employed for every 1 mol of carboxyl group present. The generation of a carboxylate in the resin may be confirmed by an IR spectrum.

Any divalent metal oxide or divalent metal hydroxide is acceptable as the divalent metal oxide or divalent metal hydroxide used in the present invention, but an oxide or hydroxide of copper, zinc, calcium, magnesium or iron is preferred at least in part from the viewpoint of costs, toxicity, reactivity and the like.

Any resins having a carboxyl group in the molecule, such as polyesters, polyurethanes, natural resin and vinyl polymers are acceptable as the resin having a carboxyl group in the molecule used in the present invention, but vinyl polymers are preferred at least in part from the

viewpoint of the freedom of changing composition and versatility. Average molecular weight of the resin can be 1,000 to 100,000, preferably, 1,500 to 50,000. The resin may contain one carboxyl group per molecule if it has a low molecular weight (e.g. 1,000 - 1,500). If the resin has a high molecular weight (e.g. 1,500 - 100,000), an acid value of 30 to 300 is preferred. In addition, for resins having a high molecular weight, there are preferably at least two carboxyl groups per molecule.

A method for producing a resin composition according to the present invention comprises the steps of adding preferably 0.5 to 5% by weight of water and a divalent metal oxide or divalent metal hydroxide to be polymerized to a resin having at least one carboxyl group. The components are preferably reacted at 50 to 200°C for preferably 1 to 20 hours. The reaction temperature and times may vary depending on many factors such as environmental factors and the desired properties of the final product. If the system becomes turbid due to the presence of water, a small amount of a polar solvent may be added. Illustrative examples of the polar solvent include solvents based on alcohols such as n-butanol and isopropyl alcohol. In addition, solvents based on ketones such as methyl ethyl ketone and methyl isobutyl ketone or solvents based on esters such as ethyl acetate, butyl acetate and isobutyl acetate may be employed. Similarly solvents based on ethers, such as CELLOSOLVE, butyl CELLOSOLVE, diethylene glycol, diethylene glycol monoethylether and diethylene glycol monobutylether are also suitable. It should be noted that a powder metal compound may not dissolve at an initial phase of the reaction, but the reaction mixture will be likely to become transparent as the reaction proceeds.

The present invention is described in detail with

reference to the following examples.

Example 1

8 g of zinc oxide, 5 g of butanol and 1 g of water were added to butyl acetate solution of 50% by weight of a copolymer having a number average molecular weight of 10,000 and consisting of 7.2 parts by weight of acrylic acid, 50 parts by weight of methyl methacrylate and 42.8 parts by weight of ethyl acrylate and these substances were caused to react at 120°C for 10 hours to obtain a transparent resin solution having a solid content of 49.2 % by weight. It was confirmed by an IR spectrum that the absorption of zinc carboxylate appeared remarkably at 1,630 cm^{-1}.

Example 2

Succinic anhydride was added to 100 g of a polyester resin having a hydroxyl group at a terminal thereof and comprising adipic acid, neopentyl glycol and trimethylol propane to obtain a polyester resin having a number average molecular weight of 3,500 and an acid value of 56. To this resin were added 100 g of CELLOSOLVE, 2 g of calcium hydroxide and 2 g of water and these substances were caused to react at 100°C for 10 hours to obtain a transparent resin solution having a solid content of 50.0 % by weight. It was confirmed by an IR spectrum that the absorption of calcium carboxylate appeared remarkably at 1,560 cm^{-1}.

Application Example

Each of the resin solutions obtained in Examples 1 and 2 was applied to an aluminum plate and dried so that the thickness of the dried film was 100 μm. The coated aluminum plate was placed at a depth of 1 m in the sea of the Suruga Bay. The coated aluminum plate was picked up

after summer was over and no barnacles clinging to the plate were observed.

For comparison, plates coated with the resins before reaction with the metal compounds of Examples 1 and 2 experienced the dissolution of the resins and had many barnacles as large as 0.5 to 3 mm clinging thereto.

Similarly, uncoated aluminum plates had many barnacles as large as 0.5 to 3 mm clinging thereto.

The resin obtained by the present invention has an excellent stainproofing function and is suitably used in stainproof coatings.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification be considered as exemplary only, with the scope of the invention being indicated by the following claims.

CLAIMS:

1. A stainproof resin composition comprising as an active ingredient, a resin having at least one metal carboxylate group represented by the following formula:

Rp-COO-M-OH (A)

wherein Rp is a substrate resin and M is a divalent metal atom.

2. The resin composition of claim 1, wherein the divalent metal atom comprises at least one metal selected from copper, zinc, calcium, magnesium and iron.

3. The resin composition of claim 1 or 2 wherein the substrate resin is a vinyl polymer having an acid value of 30 to 300.

4. A method for producing a stainproof resin composition comprising as an active ingredient a resin having at least one metal carboxylate group represented by the following formula:

Rp-COO-M-OH (A)

wherein Rp is a substrate resin and M is a divalent metal atom, the method comprising reacting a resin having at least one carboxyl group with a divalent metal oxide or a divalent metal hydroxide in the presence of water.

5. The method for producing a stainproof resin composition according to claim 4, wherein the divalent metal atom comprises at least one metal selected from copper, zinc, calcium, magnesium and iron.

6. The method for producing a stainproof resin composition according to claim 4 or 5, wherein the

substrate resin is a vinyl polymer having an acid value of 30 to 300.

7. A stainproof resin composition as claimed in claim 1 substantially as hereinbefore described in Example 1 or Example 2.

8. A method of producing a stainproof resin composition as claimed in claim 4 substantially as hereinbefore described in Example 1 or Example 2.

9. An article when coated with the stainproof resin composition as claimed in any one of claims 1, 2, 3 or 7, or when produced by a method as claimed in any one of claims 4, 5, 6 or 8.

The Patent Office

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Application No: GB 9605268.3 **Examiner:** Alan Kerry
Claims searched: 1-9 **Date of search:** 26 July 1996

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3J JCH; C3R RJ

Int Cl (Ed.6): C08F 8/42, C08F8/44; C08G 63/91

Other: Online databases: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	US 5319018	(ROHM & HAAS) see Claims 1-3, Examples	4
A	US 4870197	(EXXON) see Claims 1, 6, 7, 15, 16	4

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.